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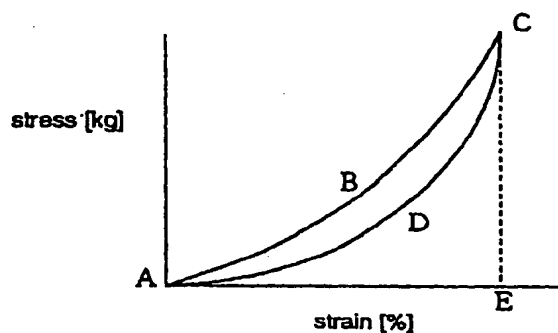
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(54) **SURFACE-DECORATED FOAM SKIN OF CROSS-LINKED RUBBERY SOFT OLEFIN RESIN**

(57) A surface decorated foam skin of cross-linked rubbery soft olefin resin, comprising rubbery soft olefin resin, characterizing by having

- (1) an average cell diameter of 50 to 400 μm ,
- (2) a crystallinity of 5 to 40%
- (3) a hysteresis loss of 35% or lower, and
- (4) an embossing percentage of 40% or higher.

Fig.1



EP 1 090 950 A1

Description

FIELD OF THE INVENTION

5 [0001] The present invention relates to a foam skin of cross-linked rubbery soft olefin resin whose surface is decorated likely as a leather or a cloth having silver like tone, that is, the surface of which is decorated using a mold which has embossed pattern or network pattern. More in detail relates to the rubbery olefin type cross-linked foam with soft resin surface layer having good heat resistance, soft touch and rubbery elasticity.

10 DESCRIPTION OF PRIOR ART

[0002] In general, the foam whose surface is decorated was existent. Among the olefin type foam, polyethylene foam can be decorated by an embossed type mold. However, the surface layer of surface part is melted, re-solidified and becomes fine (because it is high crystalline type resin). And the feeling of it is dry and rough and it is difficult to
15 obtain a feeling of leather like or cloth like. To provide a finer and deeper embossed pattern on the surface, it is necessary to intensify the heat melting condition of the surface, however, since the heat resistance of it is low (because the melting point of polyethylene is low, 100 to 120°C), shrinking ratio by heating is big and the embossing by good dimensional stability is impossible.

[0003] The foam composed by a copolymer of ethylene - vinyl acetate have a little softness, however, the heat resistance of it is inferior to that of polyethylene foam, and has a tendency to be hardened by the heating of emboss processing. Therefore, said foam is not a suited material to provide a fine and deep emboss pattern on it.

[0004] Polypropylene type foam has a good heat resistance, and therefore has a merit that the ordinary type of molding technique can be applied. However, it is a hard material, and when the surface is decorated, the surface becomes too fine and the impression of hard is emphasized.

25 [0005] And if the surface of said kinds of foams whose surface is decorated are heated to the temperature higher than the melting point to improve the transcribed ratio of grained pattern at the emboss processing, it loses its cushion feeling and becomes creased when it is bent, and is far from the feeling of leather like or cloth like, because the viscosity of these materials falls down suddenly and the permanent deformation of foam layer under the decorated surface becomes big at the emboss processing (pressed).

30 [0006] As mentioned above, the olefin foam whose surface is decorated was developed and on the market, however the applications of it are for example, a surface material of mold for an engineering works or inside materials for waterproof sheet, and cannot be used as the surface materials for interior decorations.

[0007] Meanwhile, as olefin type foam which has soft touch and rubbery elasticity, an olefin type rubber foam which uses EPR or EPT as a starting materials can be mentioned, which has a good feeling as a foam. However, since this
35 rubber foam is rubber foam which has rubber elasticity caused by a bridged material of non-crystalline rubber molecular, is a very difficult materials for surface decoration (embossing) processing. Further, since the shrinking ratio of it by heating is high, the productivity as the materials of surface sheet in a case of after decoration of foam, and is a problem.

[0008] Rubber foams except olefin type, especially in a case of chloroprene rubber foam which has excellent soft feeling, besides the ordinary problems which EPR or EPT foams have, chlorine type toxic gas generates at the heating
40 of after decoration process, which is a serious environmental problem for the corrosion of a equipment and for a human body.

[0009] As the method to solve these mentioned problems and to obtain a surface decorated olefin type foam which has good heat resistance, softness and rubbery elasticity, methods disclosed in Japanese Patent Laid Open Publication 57-20334 or in Japanese Patent Laid Open Publication 2-258247 are well-known. These methods are the method to
45 decorate the surface by laminating a heat plastic elastomer sheet having good heat resistance, softness and rubbery elasticity on above-mentioned foams. Therefore, in these methods, plural kinds of materials such as foam, surface layer sheet and adhesive are required at need, and the manufacturing process is complicated.

[0010] Meanwhile, the method disclosed in Japanese Patent Laid Open Publication 6-278220 is the method to perform a specific grained pattern directly on soft rubber foam by heating the sliced surface of rubber foam whose base
50 material is high crystalline rubber using heat roller. This method is applying the deflecting agglutination feature at hot working of high crystalline rubber and therefore the surface grained pattern is special, however, has problems at surface toughness and heat resistance.

[0011] This invention solves the problems accompany to the prior art, and the object of this invention is to provide a new foam material which can be decorated and can be used as an interior finishing material. This material not only
55 has a good heat resistance, softness and rubbery elasticity, but also the surface of which has good heat treatment processability, and the object of this invention is to provide a surface decorated rubbery soft olefin resin cross-linked foam like surface layer.

DISCLOSURE OF THE INVENTION

[0012] The present invention provides a material to be used as a material for surface layer by an emboss process. Said material is rubbery and also has property of plastics (thermo-plastic), and uses properly cross-linked olefin type resin foam.

[0013] The important point of this invention is that a surface decorated foam skin of cross-linked rubbery soft olefin resin, comprising rubbery soft olefin resin, characterizing by having average cell diameter of 50 to 400 μm , a degree of crystallinity of 5 to 40% and a hysteresis loss of 35% or lower. Further, said surface decorated foam skin of cross-linked rubbery soft olefin resin is desirably characterized as the gel fraction is in the region of 20 to 98%, 50% compressive stress is in the region of 0.3 to 1.5kg/cm², 90°C hot dimensional shrinking ratio is smaller than 5%, and the transcribed ratio of grained pattern is smaller than 40%.

[0014] That is, the average cell size of the foam like surface layer composed by rubbery soft olefin resin of this invention is 50 to 400 μm , desirably 50 to 200 μm , degree of crystallinity is 5 to 40%, desirably 5 to 35%. When the degree of crystallinity is in this region, the foam like surface layer of this invention shows sufficient restorability, good at decorative processing and generates elastic cushioning property. And by making hysteresis loss smaller than 35%, desirably smaller than 30%, and further by making the transcribed ratio of grained pattern smaller than 40%, it becomes possible to provide the surface decorated rubbery soft olefin resin cross-linked foam like surface layer which can be easily decorated by surface heat treatment of a foam maintaining good heat resistance, without spoiling softness and rubbery elasticity.

[0015] Details of the invention are illustrated as follows.

[0016] As the rubbery soft olefin resin which composes this cross-linked foam, olefin type copolymer rubber or the mixture of crystalline polyolefin resin and olefin type copolymer rubber can be used.

[0017] Said mixture of crystalline polyolefin resin and olefin type copolymer rubber has a good rubbery elasticity, and when the mixture is used as the rubbery soft olefin resin, the rubbery soft olefin resin cross-linked foam like surface layer which generates excellent restorability by rubbery elasticity can be obtained at each molding process.

[0018] The olefin type copolymer rubber of this invention is an amorphous elastic copolymer whose contents of α -olefin of carbon number 2 to 20 is smaller than 50 mol% or an elastic copolymer whose degree of crystallinity is smaller than 50%, that is, non conjugated copolymer by non crystalline α -olefin composed by more than two kinds of α -olefin, and more than two kinds of α -olefin.

[0019] As a concrete example of such kind of olefin type copolymer rubber, following kinds of rubber can be mentioned.

(1) Ethylene • α -olefin copolymer rubber [ethylene/ α -olefin, molar ratio = about 10/90~50/50]

(2) Ethylene • α -olefin • non-conjugated copolymer rubber [ethylene/ α -olefin, molar ratio = about 10/90~50/50]

(3) Propylene • α -olefin copolymer rubber [propylene/ α -olefin, molar ratio = about 10/90~50/50]

(4) Butene • α -olefin copolymer rubber [butene/ α -olefin, molar ratio = about 10/90~50/50]

[0020] As the concrete example of above mentioned α -olefin, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-desene, 1-undesene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosane, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 9-methyl-1-decene, 11-methyl-1-dodecene, 12-ethyl-1-tetradecene and combinations of these components can be mentioned.

[0021] As the concrete example of said non-conjugated diene, dicyclopentadiene, 1,4-hexadiene, cyclooctadiene, methylenenorbornene and ethylenenorbornene can be mentioned.

[0022] Mooney viscosity [ML1.4(100°C)] of these copolymer rubber is 10~250, desirably is 40 to 150.

[0023] Iodine number of said (2) ethylene • α -olefin • non-conjugated copolymer rubber is desirably smaller than 25.

[0024] Above mentioned olefin type copolymer rubber can exist in non foamed rubbery soft olefin resin composed by the mixture of olefin type copolymer rubber and crystalline polyolefin resin, by any possible states, e.g. non cross-linked, partially cross-linked or fully cross-linked.

[0025] Besides above mentioned olefin type copolymer rubber used in this invention, diene type rubber such as styrene • butadiene rubber (SBR), nitrile rubber (NBR), natural rubber (NR), butyl rubber (IIR), SEBS and polyisobutylene can be used.

[0026] In the mixture of olefin type copolymer rubber and crystalline polyolefin resin used in this invention, the desirable proportion of olefin type copolymer rubber to be used is bigger than 30 parts and smaller than 100 parts to 100 total parts of olefin type copolymer rubber and crystalline polyolefin resin by weight, more desirably from 50 to 100 weight parts and further desirably 65~95 weight parts.

[0027] As the crystalline polyolefin resin, α -olefin mono polymer or copolymer of carbon number 2 to 20 can be

mentioned.

[0028] As the concrete example of said crystalline polyolefin resin, following (co) polymer can be mentioned.

- (1) Ethylene mono polymer [polymer produced by both low pressure method and high pressure method can be used]
- (2) Copolymer of ethylene with smaller than 10 mole % of other α -olefin or viny) monomer such as viny) acetate or ethyl acrylate.
- (3) Propylene mono polymer.
- (4) Random copolymer of propylene with smaller than 10 mole % of other α -olefin.
- (5) Block copolymer of propylene and smaller than 30 mole % of other α -olefin.
- (6) 1-butene mono polymer.
- (7) Random copolymer of 1-butene mono polymer and smaller than 30 mole % of other α -olefin.
- (8) 4-methyl-1-pentene mono polymer.
- (9) Random copolymer of 4-methyl-1-pentene and smaller than 30 mole % of other α -olefin.

[0029] As a concrete example of above mentioned α -olefin composing said same α -olefin as to afore mentioned α -olefin type copolymer can be mentioned.

[0030] In the mixture of olefin type copolymer rubber and crystalline polyolefin resin used in this invention, the desirable proportion of crystalline polyolefin resin is smaller than 70 weight parts to 100 total weight parts of olefin type copolymer rubber and crystalline polyolefin resin, more desirably smaller than 50 weight parts and further desirably 5 to 35 weight parts.

[0031] As a reformer of said mixture of olefin type copolymer rubber and crystalline polyolefin resin, styrene-butadiene rubber, polybutadiene rubber, polyisoprene rubber or hydrogenated type rubber of these rubber and chlorinated polyethylene can be added by the proportion smaller than 10 weight % to 100 total weight % of olefin type copolymer rubber and crystalline polyolefin resin.

[0032] As a softener used for this mixture, paraffin type, naphthene type or aromatic type softener or an ester type plasticizer can be added by the proportion smaller than 10 weight % to 100 total weight % of olefin type copolymer rubber and crystalline polyolefin resin.

[0033] As mentioned above, since the foam of this invention is the cross-linked foam of rubbery soft-olefin resin, generally a cell forming agent and a cross-linking agent are blended.

[0034] Meanwhile, when the cross-linking reaction of resin is made by the exposure of an ionizing radiation such as electron beam, neutron beam, α -rays, β -rays, γ -rays, X-rays or ultraviolet rays, it is not necessary to blend the cross-linking agent. However, at the cross-linking reaction by the exposure of an ionizing radiation, a multi functional methacrylate monomer such as divinylbenzene, triallylcyanurate, ethyleneglycol dimethacrylate, trimethylolpropane trimethacrylate or acrylicmethacrylate, or a multi functional vinyl monomer such as vinylbutylate or vinylstearate can be added as a cross linking promoter. By blending said cross-linking promoter, gel fraction can be adjusted.

[0035] As the cell-forming agent to be used in this invention, a heat decomposing type cell forming agent which generates gas by heat decomposition is desirably used. As the concrete example, diethylazocarbonamide, azodicarbonamide, barium azodicarboxylate, 4,4-oxybis(benzenesulfonylhydrazide), 3,3-disulfonehydrazidephenylsulfonic acid and N,N-dinitropentatetramine can be mentioned.

[0036] Ordinary, the cell forming agent is added by the proportion of 3 to 25 weight parts to 100 weight part of the matrix of unformed rubbery soft olefin resin, desirable proportion to be added is 5 to 20 weight parts and more desirable proportion to be added is 7 to 15 weight parts.

[0037] These cell forming agents can be used alone or by the combination of more than two types, further so called decomposing promoting agent can be used together with.

[0038] Further, the cell of resin foam can be generated by the vapor pressure of volatile solvent or water, instead of cell forming by the cell-forming agent

[0039] The cross-linking reaction of this invention can be carried out by the well-known cross-linking method. As the typical example which uses cross-linking agent, a cross-linking by vulcanization and a cross-linking by peroxide can be mentioned.

[0040] And also the cross-linking by ionizing radiation can be carried out by the well-known cross-linking method.

[0041] The desirable cross-linking agent to be used in the method by peroxide is organic peroxide, and as the concrete example,

dicumylperoxide,
di-tert-butylperoxide,
2,5-dimethyl-2,5-di (tert-butylperoxy)hexane,
2,5-dimethyl-2,5-di (tert-butylperoxy)hexine-3,

1,3-bis(tert-butylperoxyisopropyle)benzene,
 1,1-bis(tert-butylperoxy)-3,3,5-trimethylsyclohexane,
 n-butyl-4,4-bis(tert-butylperoxy)valerate,
 benzoylperoxide,
 5 p-chlorbenzoylperoxide,
 2,4-dichlorobenzoylperoxide,
 tert-butylperoxybenzoate,
 tert-butyloxyisopropylecarbonate,
 diacetylperoxide, lauroilperoxide and
 10 tert-butylcumylperoxide can be mentioned.

[0042] Among these compounds,

2,5-dimethyl-2,5-di (tert-butylperoxy) hexane,
 15 2,5-dimethyl-2,5-di (tert-butylperoxy)hexine-3,
 1,3-bis(tert-butylperoxyisopropyl)benzene,
 1,1-bis(tert-butylperoxy)-3,3,5-trimethylsyclohexane and
 n-butyl-4,4-bis(tert-butylperoxy)valerate can be desirably used from the view point of bad odor and scorching sta-
 bility, and
 20 1,3-bis(tert-butylperoxyisopropyl) benzene is most desirably used.

[0043] The desirable blending ratio of organic peroxide is 0.5 to 2.5 weight parts to 100 weight parts of un-foamed rubbery soft olefin resin matrix, and the substantial blending ratio is determined concerning cell size of foam, gel frac-
 tion and density.

25 [0044] In the present invention, as the cross-linking process by said peroxide, peroxy cross-linking promoting agent such as sulfur, p-quinonedioxime, p,p'-benzoylquinonedioxime, N-methyl-N-4-dinitrosoaniline, nitrosobenzene, diphe-
 nylguanidine, trimethylolpropane or N,N'-m-phenylenedimaleimide, or a multi-functional methacrylate monomer such as divinylbenzene, triallylcyanurate, ethyleneglycol dimethacrylate, trimethylolpropane, trimethacrylate or acrylicmeth-
 acrylate, or a multi functional vinyl monomer such as vinylbutylate or vinylstearate can be blended.

30 [0045] By blending of said cross-linking promoter, gel fraction can be adjusted.

[0046] To the rubbery soft olefin resin of this invention, additives which are ordinary used to the olefin type thermo-
 plastic elastomer composition such as cross-linking agent, cross-linking promoter, cell forming promoter, weather
 resistance stabilizer, heat resistance stabilizer, plasticizer, fire retardant, viscosity increasing agent, slipping agent, and
 pigments can be added at need within the limit not to hurt the object of this invention.

35 [0047] Furthermore, filler can be blended to said rubbery soft olefin resin can be added. As the concrete example
 of the filler, an organic filler such as carbon black, nitroso pigment, colcothar, phthalocyanine pigment, pulp, fiber like
 chip or agar-agar and an inorganic filler such as clay, kaoline, silica, diatomaceous earth, aluminum hydroxide, zinc
 oxide, magnesium hydroxide, titanium oxide, mica, bentonite, sirasu balloon, zeolite, silicate white earth, cement, and
 silica fume can be mentioned.

40 [0048] The cross-linked foam like surface layer of rubbery soft olefin resin.

[0049] Said foam like surface of this invention is a cross-linked foam of rubbery soft olefin resin composed by above
 mentioned components, and desirable cell size of it is 50 μm to 400 μm and more desirably 50 μm to 200 μm .

[0050] The degree of crystallinity determined by an X-ray diffraction method of the mixture of polyolefin resin and
 rubber composing said foam like surface layer of this invention which is prepared as mentioned above is desirably to be
 45 within the region of 5 to 35% and more desirably 6 to 25%.

[0051] Further, the hysteresis loss of the cross-linked foam of rubbery soft olefin resin which composes the foam
 like surface layer of this invention prepared as above is desirably smaller than 35%, more desirably smaller than 30%.

[0052] When the cell size, degree of crystallinity and hysteresis loss of the cross-linked foam like surface layer of
 rubbery soft olefin resin are within the region mentioned above, the heat treatment processability of foam like surface
 50 layer is very good and has good heat resistance and can generate a softness and a rubber elasticity. In the meanwhile,
 the method to measure the cell size, degree of crystallinity by X-ray diffraction method and hysteresis loss is disclosed
 in Example of this invention.

[0053] Additionally, the gel fraction of the cross-linked foam like surface layer of rubbery soft olefin resin is 20 to
 98% and desirably 40 to 90%. When the gel fraction is within the above-mentioned limit, the heat treatment processa-
 55 bility of foam like surface layer is very good and has good heat resistance and can generate softness and rubber elas-
 ticity.

[0054] Further, the 50% compressive stress of the cross-linked foam like surface layer of rubbery soft olefin resin
 of this invention is 0.3 to 1.5kg/cm² and desirably 0.3 to 1.0 kg/cm², furthermore, the 90°C hot dimensional shrinking

ratio is smaller than 5% and desirably smaller than 3%. When the 50% compressive stress and 90°C hot dimensional shrinking ratio are within the above mentioned limit, the heat treatment processability of foam like surface layer is very good and has good heat resistance and can generate a softness and a rubber elasticity.

[0055] The method for preparation of the cross-linked foam like surface layer of rubbery soft olefin resin.

[0056] The cross-linked foam like surface layer of rubbery soft olefin resin of this invention can be prepared by the following method.

[0057] As the first step, all components mentioned above are kneaded homogeneously and non-foamed non cross-linked rubbery soft olefin resin is prepared and the resin is molded to a desired shape.

[0058] As the method to prepare non foamed non cross-linked rubbery soft olefin resin, for example, the method to fuse and knead a heat decomposition type cell forming agent, a cross-linking agent and other additives separately into the mixture (matrix) composed by olefin type copolymer rubber and crystalline polyolefin resin or olefin type copolymer rubber (matrix) can be mentioned.

[0059] In this method, for instance, olefin type copolymer resin and crystalline polyolefin resin are kneaded by a well-known kneader such as V type brabender, tumble brabender, ribbon brabender, Henshel brabender and further kneaded by an extruder, mixing roller, kneaded or Bumbury's mixer.

[0060] This kneading process is desirably to be carried out at the temperature lower than decomposing temperature of the heat-decomposing cell forming agent.

[0061] The cell forming promoter, wetting agent, weather resistance stabilizer, heat-resistance stabilizer, anti-aging agent and pigments can be blended at any melting kneading process.

[0062] Then, to the kneaded product obtained by mentioned kneading process, a cross-linking agent and cross-linking promoting agent and a vulcanization promoting agent are added and kneaded by a well-known kneader such as V type brabender, tumble brabender, ribbon brabender, Henshel brabender at desirably lower temperature than decomposing temperature of cross-linking agent (50°C), then the kneaded product is added to a conventional well-known kneader such as open type mixing roller, not-open type Bumbury's mixer, extruder, kneader or continuous mixer and said cross-linking agent and other agents are dispersed.

[0063] Said kneading process is carried out at the lower temperature than the decomposition temperature of a heat decomposing type cell forming agent and a cross-linking agent, and desirable temperature is 20 to 50 °C lower temperature than one-minute half-time temperature of the cross-linking agent.

[0064] As the another preparing method of non foamed non cross-linked rubbery soft olefin resin, the method to add a heat decomposing cell forming agent, a cross-linking agent and other additives simultaneously to olefin type copolymer rubber and crystalline polyolefin resin and to melt and knead can be mentioned.

[0065] In above mentioned method, olefin type copolymer rubber; pellets of crystalline polyolefin resin, and additives such as heat decomposing cell forming agent and cross-linking agent are continuously kneaded at lower temperature than the decomposing temperature of the heat decomposing cell forming agent and cross-linking agent using for example double shaft extruder.

[0066] Then, the obtained non-foamed non cross-linked rubbery soft olefin resin is formed to a sheet shape at the temperature which the heat decomposing cell forming agent and cross-linking agent does not decompose, and non cross-linked, non-foamed sheet type product can be obtained.

[0067] Said forming can be carried out by conventional well-known forming machine such as heat press or calendar roll.

[0068] Further, in the present invention, melting and kneading of olefin type copolymer rubber and crystalline polyolefin resin, melting and kneading of obtained mixture with a heat decomposing cell forming agent and a cross-linking agent and a procedure to obtain non cross-linked, non-foamed soft resin, can be carried out by series using a molding machine such as single shaft extruder or double shaft extruder.

[0069] The foam like surface layer of rubbery soft olefin resin can be obtained by processing said formed product of non cross-linked, non-foamed soft resin obtained by above-mentioned procedure. The formed sheet is provided to a continuous heat double press belt which has specific same height brims on both width end or stuffed into a specific mold, heat pressed at higher temperature than 130°C (desirably 140°C to 230°C) and higher pressure than 40kg/cm² (desirably 60kg/cm² to 150kg/cm²) for fixed time and then release the pressure, or after the heat pressure the un-foamed or the half foamed imperfect foam is secondary foamed at atmosphere pressure, thus the foam like surface layer of rubbery soft olefin resin can be obtained.

[0070] In a case of foaming at atmosphere pressure, un-foamed product is heated by a conventional well-known method such as hot air circulating, salt bath heating, radio-frequency heating, infra red rays heating and heat press and a cross-linking agent and heat decomposing foaming agent contained in un-foamed product are decomposed by heat, thus the foam like surface layer of rubbery soft olefin resin of this invention can be obtained.

[0071] Among the above mentioned preparation method, the most desirable method is mentioned as follows. That is, the heat pressure is made for fixed time then release the pressure and obtain the foam like surface layer of rubbery soft olefin resin of this invention directly, or the un-foamed or the half foamed imperfect foam is secondary foamed at

atmosphere pressure, and obtain the cross-linked foam like surface layer of rubbery soft olefin resin.

[0072] At the above-mentioned foaming process or just after the foaming, the specific pattern can be provided on the surface of foam and further the surface toughness can be improved by stamping of pattern.

[0073] The cross-linked foam like surface layer of rubbery soft olefin resin of this invention is composed by a rubbery soft olefin resin, and is the cross-linked foam like surface layer of rubbery soft olefin resin of

- (1) average cell size is 50 μm to 400 μm ,
- (2) degree of crystallinity of the foam is 5 to 40%,
- (3) hysteresis loss is smaller than 35%, and
- (4) gel fraction is 20 to 98%,
- (5) 50% compressive stress is 0.3 to 1.5kg/cm² and 90°C hot dimensional shrinking ratio is 5 to 40%,

has especially excellent processability of the surface of foam, has good heat resistance, has softness and rubber elasticity like fabrics or cloth and can obtain a decorated foam having an appearance of synthetic leather.

[0074] Concretely, as the heat treatment method of the foam surface, the surface of foam obtained by above mentioned method, desirably the surface of sliced foam is held and pressed between heat rollers or a heat press, or by a vacuum forming (concave mold) and the smoothness and the toughness of the foam surface is remarkably improved. By engraving a grained pattern on the surface of roller, presser or a mold of vacuum forming (concave mold) and transcribe the pattern to the surface of foam, softness and rubbery elasticity can be generated on the surface of foam.

[0075] As the more desirable processing method of the foam surface, the following method can be mentioned. That is, before the pressing by rollers or a presser or a vacuum forming, the surface of foam is previously heat treated by flame, infrared rays or hot air, then cold or hot pressed or formed by vacuum forming, and the surface of the cross-linked foam like surface layer of rubbery soft olefin resin is processed like a leather.

[0076] When a grained pattern or a network pattern is provided to the material of this invention, even if the mold compressive ratio is closely to 10% the material is not crushed because it has a good restoration ability, and profound emboss like or cloth like pattern can be provided. This phenomenon cannot be expected to the conventional olefin type foam. For example, after the surface of a conventional polyethylene foam is heat treated, when compressive ratio at cold press is raised, the foam is crushed remarkably and violently curled and good decorated foam cannot be obtained.

[0077] These kinds of surface treatment process can be made continuously or by batch processing. And the cross-linked foam like surface layer of rubbery soft olefin resin on which the combination surface treatment process with a coating or a printing is possible can be provided.

[0078] In the cross-linked foam like surface layer of rubbery soft olefin resin of this invention, the state of reverse side is not limited. The reverse side can be the foam itself or can be laminated to cloth, un-woven cloth or sheet of thermo-plastic resin.

BRIEF ILLUSTRATION OF DRAWINGS

[0079]

Fig.1 is a drawing indicates a hysteresis curve to measure the hysteresis loss of the foam of this invention.

Fig.2 is a mold used to measure the transcribed ratio of grained pattern of the foam of this invention.

Fig.3 is the schematic view of microscopic observation showing transcript of grained pattern by use of the mold of Fig.1

a shows the case of good transcript ratio.

b is the case showing that the transcript ratio is not good (showing the case in which the foam is hard and edge is dulled, and in this case $W > W'$)

c is the case showing that the transcript ratio is not good (showing the case in which permanent deformation at the pressing process is big, and in this case $H > H'$)

d is the case showing that the transcript ratio is not good (showing the case in which the foam shrinks by the influence of the preheating at the pressing process, and in this case $P > P'$ and $W > W'$)

THE BEST EMBODYMENT TO CARRYOUT THE INVENTION

[0080] The present invention is illustrated by the Examples, however, not intended to be limited to them.

[0081] In the Examples and Comparative Examples, density of a foam (g/cm³), average cell size (mm) and degree of crystallinity (%) are measured by following methods.

(measuring method)

(1) density (g/cm³)

- 5 [0082] Specimen of 10cm × 10cm square is cut from the sheet of foam of thickness t(cm), and the weight (W[g]) of the specimen is weighted and the density (g/cm³) is calculated by following numerical formula.

$$\text{density (g/cm}^3\text{)} = W/(t \times 10 \times 10)$$

10 (2) average cell size

[0083] Numbers of cells (n) per 3.3mm square are counted by a microscope of 60 magnification, and the average cell size (mm) is calculated by following numerical formula.

15
$$\text{average cell size (mm)} = \sqrt{(3.3)/\pi \cdot n}$$

(3) degree of crystallinity

- 20 [0084] Measured by a wide-angle X-ray diffraction (signal intensity[CPS] · · · 2θ [3° < 2θ < 40°]), total signal area belonging to crystalline is divided by total signal area belonging crystalline and amorphous state and expressed by %. This value is indicated as the crystalline

(4) hysteresis loss (%)

- 25 [0085] Specimens of 5cm × 5cm square are cut from the sheet of foam of thickness t(cm), and the specimens are piled up and adjusted to 2.5mm thickness and prepare a specimen for the measurement. Said prepared specimen is pressed by 50mm/min compressive speed at room temperature using a compression tester and the hysteresis at room temperature is measured. The compressive ratio is 50% to the original thickness. The obtained hysteresis curve at above mentioned condition is recorded to the recording paper is shown in FIG.1, and the hysteresis loss is measured
30 by following numerical formula.

$$\text{hysteresis loss (\%)} = (S1/S0) \times 100$$

wherein,

- 35 S1: area surrounded by curve B and curve D
S0: area surrounded by curve B, curve AE and Curve CE

(5) gel fraction (%)

- 40 [0086] A foam pad is cut to 1mm square specimen chips, contained into a Soxhlet extractor and oil in specimen is extracted by chloroform. The foam pad specimen after extracted is dried up by vacuum and 0.2g (W0 [g]) of specimen is weighted. The weighted specimen is dissolved into 500ml of 130°C heated xylene for 6 hours and xylene soluble parts are extracted from the specimen. The xylene insoluble part is rinsed by acetone and dried up in 100°C vacuum
45 dryer for 1 hour. After dried up, the xylene insoluble part is weighted (W1 [g]) and gel fraction (%) is calculated by following numerical formula.

$$\text{gel fraction (\%)} = (W1/W0) \times 100$$

50 (6) 50% compressive hardness [kg/cm²]

[0087] 50% compressive hardness [kg/cm²] at 25°C is measured in accordance with the measuring method of JISK-6767.

55 (7) hot dimensional shrinking ratio (%)

[0088] hot dimensional shrinking ratio at 90°C is measured in accordance with the measuring method of JISK-6767.

(8) transcribed ratio of grained pattern (%)

[0089] Grained pattern is transcribed over the surface of a foam using a concave mold with 1.0mm width (W), 1.0mm depth (d), 2.0mm pitch (p) grit pattern (groove) illustrated by FIG.2. After processed, the foam is cut along with the grit mark and the height of grained pattern (H) and pitch (P) are observed by a microscope, and transcribe ratio of grained pattern (%) is calculated by following numerical formula.

$$\text{transcribed ratio of grained pattern (\%)} = [\text{height(H)} + \text{pitch (P)}] \times 100/3$$

[0090] Substantial examples indicating several transcribed pattern are shown in FIG.3.

a shows the case of good transcript ratio.

b is the case showing that the transcript ratio is not good (showing the case in which the foam is hard and edge is dulled, and in this case $W > W'$)

c is the case showing that the transcript ratio is not good (showing the case in which permanent deformation at the pressing process is big, and in this case $H > H'$)

d is the case showing that the transcript ratio is not good (showing the case in which the foam shrinks by the influence of the preheating at the pressing process, and in this case $W > W'$ and $P > P'$)

Example 1

[0091] To 100 weight parts of the mixture composed by 60 weight % of ethylene • propylene • non-conjugated copolymer rubber [EPT ; 38mol% ethylene content Iodine number 12, MFR(ASTM 1238, 190°C, 2.16kg load) 1.1g/10 min], 20 weight % of polyethylene [PE ; 100mol% ethylene content, MFR(ASTM 1238, 190°C, 2.16kg load) 1.6g/10min] and 10 weight % of polypropylene [PP ; 100% propylene content, MFR(ASTM 1238, 190°C, 2.16kg load) 5.0g/10min], 10 weight parts of azodicarbonamide [ADCA ; pore forming agent], 1.2 weight parts of 2,5-dimethyl-2,5-di(tert-dibutyl peroxi) hexine-3 [peroxide cross-linking agent] and 0.3 parts of trimethylolpropane -trimethacrylate [TMPT ; cross-linkage promoting agent] are added and kneaded by a roller mixer and non-cross-linked, non-foamed composition is obtained.

[0092] Then, the resin composition is poured into the mold of 3mm thickness and heat pressed at 210°C, 100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.058g/cm³ and thickness is 8.7mm. This cross-linked foam skin is a foam of 80 μm average cell size, 8% degree of crystallinity, 20% hysteresis loss, 77.0% gel fraction, 650g/cm² 50% compressive stress and 3.3% hot dimensional shrinking ratio at 90°C, 22 hours.

[0093] Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved at compressive ratio 50% and 90%. The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern is clearly transcribed (transcribed ratio of grained pattern, 91% and 96%). After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result of 600 g/cm² and 1.1% can be obtained. Thus, the cross-linked foam like surface layer of rubbery soft olefin resin with smooth and tough skin layer and grained pattern whose heat resistance and softness is good can be obtained.

Example 2

[0094] To 100 weight parts of the mixture composed by 60 weight parts of ethylene • propylene • non-conjugated copolymer rubber [EPT], 20 weight % of polyethylene [PE] and 10 weight % of polypropylene [PP] of Example 1, 3 weight parts of azodicarbonamide [ADCA ; pore forming agent], 1.2 weight parts of 2,5-dimethyl-2,5-di(tert-dibutyl peroxi) hexine-3 [peroxide cross-linking agent] and 0.3 parts of trimethylolpropanetrimethacrylate [TMPT ; cross-linkage promoting agent] are added and kneaded by a double shaft kneading extruder at 120°C and non-cross-linked, non-foamed composition is obtained.

[0095] Then, the resin composition is poured into the mold of 3mm thickness and heat pressed at 210°C, 100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.053g/cm³ and thickness is 7.2mm. This cross-linked foam skin is a foam of 95 μm average cell size, 8% degree of crystallinity, 22% hysteresis loss, 71.0% gel fraction, 980g/cm² 50% compressive stress and 3.5% hot dimensional shrinking ratio at 90°C, 22 hours.

[0096] Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved at the compressive ratio 50% and 90%.

The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern is clearly transcribed (transcribed ratio of grained pattern, 83% and 93%). After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result of 970 g/cm² and 1.3% can be obtained. Thus, the cross-linked foam like surface layer of rubbery soft olefin resin with smooth and tough skin layer and grained pattern whose heat resistance and softness is good can be obtained

Example 3

[0097] To 100 weight parts of the mixture composed by 65 weight parts of ethylene • propylene • non-conjugated copolymer rubber [EPT] and 10 weight % of polypropylene [PP] of Example 1, 6 weight parts of azodicarbonamide [ADCA; cell forming agent], 0.7 weight parts of 2,5-dimethyl-2,5-di(tert-dibutyl peroxy) hexine-3 [peroxide cross-linking agent], 0.7 parts of trimethylolpropane-trimethacrylate [TMP; cross-linkage promoting agent] and 1.0 part of zinc oxide are added and kneaded by a roller mixer at 120°C and non-cross-linked, non-foamed composition is obtained.

[0098] Then, the resin composition is poured into the mold of 3mm thickness and heat pressed at 165°C, 100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.047g/cm³ and thickness is 8.7mm. This cross-linked foam skin is a foam of 58 μm average cell size, 27% degree of crystallinity, 25% hysteresis loss, 65.0% gel fraction, 750g/cm² 50% compressive stress and 2.5% hot dimensional shrinking ratio at 90°C, 22 hours.

[0099] Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved at compressive ratio 50% and 90%. The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern is clearly transcribed (transcribed ratio of grained pattern, 91% and 96%). After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result of 730 g/cm² and 0.7% can be obtained. Thus, the cross-linked foam like surface layer of rubbery soft olefin resin with smooth and tough skin layer and grained pattern whose heat resistance and softness is good can be obtained

Example 4

[0100] To 100 weight parts of the mixture composed by 60 weight parts of ethylene • propylene • non-conjugated copolymer rubber [EPT], 10 weight % of polyethylene [PE] and 20 weight % of polypropylene [PP] of Example 1, 6 weight parts of azodicarbonamide [ADCA ; pore forming agent], 1.4 weight parts of 1,3bis(tert-buthylperoxyisopropyle)benzene [peroxide cross-linking agent], 0.3 parts of trimethylolpropanetrimethacrylate [TMPT ; cross-linkage promoting agent], 0.5 weight parts stearic acid (slipping agent) and 1.0 part of zinc oxide are added and kneaded by a roller mixer at 120°C and fed out as a sheet by a roller and non-cross-linked, non-foamed composition is obtained. Then, the resin composition is poured into the mold of 3mm thickness and heat pressed at 165°C, 100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.049g/cm³ and thickness is 8.7mm. This cross-linked foam skin is a foam of 64 μm average cell size, 16% degree of crystallinity, 21 % hysteresis loss, 76.0% gel fraction, 690g/cm² 50% compressive stress and 1.5% hot dimensional shrinking ratio at 90°C, 22 hours.

[0101] Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved at compressive ratio 50% and 90%. The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern is clearly transcribed (transcribed ratio of grained pattern, 86% and 93%). After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result of 660 g/cm² and 0.9% can be obtained. Thus, the cross-linked foam like surface layer of rubbery soft olefin resin with smooth and tough skin layer and grained pattern whose heat resistance and softness is good can be obtained

Example 5

[0102] To 100 weight parts of the mixture composed by 60 weight parts of ethylene • propylene • non-conjugated copolymer rubber [EPT] and 30 weight % of polypropylene [PP] of Example 1, 10 weight parts of azodicarbonamide [ADCA ; pore forming agent], 0.8 weight parts of 1,3bis(tert-buthylperoxy isopropyle)benzene [peroxide cross-linking agent], 0.8 parts of trimethylolpropane-trimethacrylate [TMPT ; cross-linkage promoting agent], 0.5 weight parts stearic acid and 1.0 part of zinc oxide are added and kneaded by a roller mixer at 120°C and fed out as a sheet by a roller and non-cross-linked, non-foamed composition is obtained.

[0103] Then, the resin composition is poured into the mold of 2mm thickness and heat pressed at 210°C,

100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.045g/cm³ and thickness is 5mm. This cross-linked foam skin is a foam of 110 μm average cell size, 21% degree of crystallinity, 20% hysteresis loss, 67.0% gel fraction, 740g/cm² 50% compressive stress and 1.0% hot dimensional shrinking ratio at 90°C, 22 hours.

- 5 **[0104]** To the obtained sheet of cross-linked foam infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved at compressive ratio 50% and 90%. The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern is clearly transcribed (transcribed ratio of grained pattern, 94% and 96%). After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result
10 of 710g/cm² and 0.8% can be obtained. Thus, the cross-linked foam like surface layer of rubbery soft olefin resin with smooth and tough skin layer and grained pattern whose heat resistance and softness is good can be obtained

Comparative Example 1

- 15 **[0105]** To 100 weight parts of ethylene-propylene non-conjugated copolymer rubber [EPT] of Example 1, 6 weight parts of azodicarbonamide [ADCA; cell forming agent], 1.2 weight parts of 2,5-dimethyl-2,5-di(tert-dibutylperoxy) hexine-3 [peroxide cross-linking agent], 0.3 parts of trimethylolpropane-trimethacrylate [TMPT; cross-linkage promoting agent], 0.5 weight parts stearic acid and 1.0 part of zinc oxide are added and kneaded by a roller mixer at 120°C and fed out as a sheet by a roller and non-cross-linked, non-foamed composition is obtained.
- 20 **[0106]** Then, the resin composition is poured into the mold of 3mm thickness and heat pressed at 165°C, 100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.070g/cm³ and thickness is 8.3mm. This cross-linked foam skin is a foam of 150 μm average cell size, 0% degree of crystallinity, 20% hysteresis loss, 90.0% gel fraction, 630g/cm² 50% compressive stress and 5.3% hot dimensional shrinking ratio at 90°C, 22 hours.
- 25 **[0107]** Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved by compressive ratio 50% and 90%. The surface of the foam faced to the flat plate is largely shrunk and hardened and becomes coarse, and to the surface of the foam faced to the plate with grained pattern the pattern the grained pattern is not transcribed (transcribed ratio of grained pattern, 8% and 13%). And after the surface heat treatment, 50% compressive stress and hot dimensional
30 shrinking ratio at 90°C, 22 hours are measured and the result of 600g/cm² and 6.1% can be obtained. Softness is good, however, the heat resistance is not good.

Comparative Example 2

- 35 **[0108]** To 100 weight polyethylene [PE] of Example 1, 6 weight parts of azodicarbonamide [ADCA; cell forming agent], 0.8 weight parts of 1,3bis(tert-butylperoxy isopropyle)benzene [peroxide cross-linking agent], 0.5 weight parts stearic add and 1.0 part of zinc oxide are added and kneaded by a roller mixer at 120°C and fed out as a sheet by a roller and non-cross-linked, non-foamed composition is obtained.
- [0109]** Then, the resin composition is poured into the mold of 3mm thickness and heat pressed at 165°C,
40 100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.045g/cm³ and thickness is 8.7mm.
- [0110]** This cross-linked foam skin is a foam of 110 μm average cell size, 55% degree of crystallinity, 55% hysteresis loss, 78.0% gel fraction, 1500g/cm² 50% compressive stress and 7.3% hot dimensional shrinking ratio at 90°C, 22 hours.
- 45 **[0111]** Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved by compressive ratio 60% and 90%. The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern seemed to be dearily transcribed, however, the transcribed ratio of grained pattern are 65% and 35%, because the shrinkage at heating process and permanent deformation at pressing process
50 are big. After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result of 1800g/cm² and 5.1% can be obtained, and the softness and heat resistance are hurt. When the surface with grained pattern is slightly fold to the inside, many creases are generated and the appearance of decorated surface is hurt.

55 Comparative Example 3

- [0112]** To 100 weight parts of ethylene vinyl acetate copolymer [EVA; 14% vinyl acetate content, MFR (JISK-6703, 190°C, 2.16 kg load) 1.3/10min], 10 weight parts of azodicarbonamide [ADCA; cell forming agent], 0.8 weight parts of

1,3bis(tert-butylperoxy isopropyle)benzene [peroxide cross-linking agent], 0.5 weight parts stearic acid and 1.0 part of zinc oxide are added and kneaded by a roller mixer at 120°C and fed out as a sheet by a roller and non-cross-linked, non-foamed composition is obtained.

[0113] Then, the resin composition is poured into the mold of 3mm thickness and heat pressed at 165°C, 100kg/cm² as to carry out cross-linking and foaming and obtained the sheet of cross-linked foam whose density is 0.045g/cm³ and thickness is 8.7mm.

[0114] This cross-linked foam skin is a foam of 80 µm average cell size, 9% degree of crystallinity, 45% hysteresis loss, 93.0% gel fraction, 1100g/cm² 50% compressive stress and 8.5% hot dimensional shrinking ratio at 90°C, 22 hours.

[0115] Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated, then cold pressed between a flat plate and a plate on which grained pattern is engraved at compressive ratio 50% and 90%. The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern is not clearly transcribed. The transcribed ratio of grained pattern are 15% and 25%, and are low level, because the diacetic acid reaction is progressed in a molecular and intermolecular cross-linking reaction is progresses at surface heating process After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result of 1500g/cm² and 10.2% can be obtained, and the softness and heat resistance are spoiled. This product has residue of odor of acetic acid.

Comparative Example 4

[0116] To 100 weight parts of the mixture composed by 20 weight parts of polyethylene [PE] and 80 weight of polypropylene [PP] of Example 1, 10 weight parts of azodicarbonamide [ADCA; cell forming agent], 5.0 weight parts of divinylbenzene [DVB; cross-linking promoting agent], are added and kneaded by a double shaft kneading extruder and extruded as a sheet and non-cross-linked, non-foamed composition is obtained.

[0117] Then, to the resin composition sheet an electron beam of 6Mrad is irradiated, and is cross-linked and foamed at atmosphere at 220°C, and the sheet of cross-linked foam whose density is 0.07g/cm³ and thickness is 8.7mm is obtained.

[0118] This cross-linked foam skin is a foam of 120 µm average cell size; 78% degree of crystallinity; 60% hysteresis loss, 64.0% gel fraction; 2100g/cm² 50% compressive stress and 1.3% hot dimensional shrinking ratio at 90°C, 22 hours.

[0119] Obtained sheet of cross-linked foam are sliced to 3mm thickness and infrared rays is irradiated) then cold pressed between a flat plate and a plate on which grained pattern is engraved at compressive ratio 50% and 90%. The surface of the foam faced to the flat plate becomes smooth surface with a skin layer, and to the surface of the foam faced to the plate with grained pattern the pattern is seemed to be clearly transcribed, however, the transcribed ratio of grained pattern are low, 64% and 43%, because after heating, the permanent deformation at pressing process are big. After the surface heat treatment, 50% compressive stress and hot dimensional shrinking ratio at 90°C, 22 hours are measured and the result of 2300 g/cm² and 0.7% can be obtained. The heat resistance is good; however, softness is hurt.

[0120] The property of surface decorated foams mentioned in Examples 1 to 5 and Comparative Examples 1 to 4 are summarized in Table 1 and Table 2.

Table 1

| properties | | Ex.1 | Ex.2 | Ex.3 | Ex.4 | Ex.5 |
|------------|---|------|------|------|------|------|
| foam | cell size (µm) | 80 | 95 | 58 | 64 | 110 |
| | crystallinity (%) | 8 | 8 | 27 | 16 | 21 |
| | hysteresis loss (%) | 20 | 22 | 25 | 21 | 20 |
| | gel fraction (%) | 77 | 71 | 65 | 76 | 67 |
| | 50% compressive hardness (g/cm ²) | 650 | 980 | 750 | 690 | 740 |
| | dimensional shrinking ratio (%) | 3.3 | 3.5 | 2.5 | 1.5 | 1.1 |

Table 1 (continued)

| properties | | Ex.1 | Ex.2 | Ex.3 | Ex.4 | Ex.5 |
|---------------------------------|---|----------|----------|----------|----------|----------|
| foam after surface heat treated | 50% compressive hardness (g/cm ²) | 600 soft | 970 soft | 730 soft | 660 soft | 710 soft |
| | dimensional shrinking ratio (%) | 1.1 good | 1.3 good | 0.7 good | 0.9 good | 0.8 good |
| | surface smoothness | good | good | good | good | good |
| | grained pattern appearance | good | good | good | good | good |
| | grained pattern transcribed ratio (%) | | | | | |
| | 50% compressed | 91 | 83 | 74 | 86 | 94 |
| | 100% compressed | 96 | 93 | 87 | 93 | 96 |

Table 2

| properties | | Co.Ex.1 | Co. Ex.2 | Co.Ex.3 | Co.Ex.4 |
|---------------------------------|---|--------------|--------------|--------------|-----------|
| foam | cell size (μm) | 150 | 110 | 80 | 120 |
| | crystalline ratio (%) | 0 | 55 | 9 | 78 |
| | hysteresis loss (%) | 20 | 55 | 45 | 60 |
| | gel fraction (%) | 90 | 78 | 93 | 64 |
| | 50% compressive hardness (g/cm ²) | 630 | 1500 | 1100 | 2100 |
| | dimensional shrinking ratio (%) | 5.3 | 7.3 | 8.5 | 1.3 |
| foam after surface heat treated | 50% compressive hardness (g/cm ²) | 600 soft | 1800 hard | 1500 hard | 2300 hard |
| | dimensional shrinking ratio (%) | 6.1 not good | 1.3 not good | 0.7 not good | 0.9 good |
| | surface smoothness | not good | good | good | good |
| | sharpness of grained pattern | not good | good | good | good |
| | grained pattern transcribe ratio (%) | | | | |
| | 50% compressed | 8 | 65 | 15 | 64 |
| | 90% compressed | 13 | 35 | 25 | 43 |

[0121] From these Examples, the cross-linked foam like surface layer of rubbery soft olefin resin of this invention

which is composed by a rubbery soft olefin resin and has properties of average cell size is 50 μm to 400 μm , degree of crystallinity of the foam is 5 to 40%, hysteresis loss is smaller than 35% and transcribed ratio of grained pattern is bigger than 40%, has a good surface smoothness, an excellent surface heat processability, a good heat resistance and softness and rubbery elasticity. Further, the decorated foam which has a leather like appearance can be obtained.

The possibility for the industrial use

[0122] As mentioned above, the cross-linked foam like surface layer of this invention, the fine and silver like surface layer can be obtained by foaming with skin and by transcribing the grained pattern and further the surface intensity is improved. On the contrary, by forming transcribed pattern and network on the sliced surface of foam, the surface layer with grained pattern or cloth pattern with good feeling. And in any case, the rubbery soft olefin resin cross-linked foam like surface layer is not creased and fine and deep pattern can be embossed, has good feeling and surface intensity can be improved. Thus the surface layer which is suited to the interior surface decoration can be provided.

Claims

1. A surface decorated foam skin of cross-linked rubbery soft olefin resin, comprising rubbery soft olefin resin, characterizing by having average cell diameter of 50 to 400 μm , a degree of crystallinity of 5 to 40% and a hysteresis loss of 35% or lower.
2. The surface decorated foam skin of cross-linked rubbery soft olefin resin of claim 1, wherein the gel fraction of said rubbery soft olefin resin is 20 to 98%.
3. The surface decorated foam skin of cross-linked rubbery soft olefin resin of claim 1, wherein the 50% compressive stress is 0.3 to 1.5 kg/cm^2 and 90% hot dimensional shrinking ratio is 5% or lower.
4. The surface decorated foam skin of cross-linked rubbery soft olefin resin of claim 1, wherein the grained pattern transcribed ratio is 40% or higher.

Fig.1

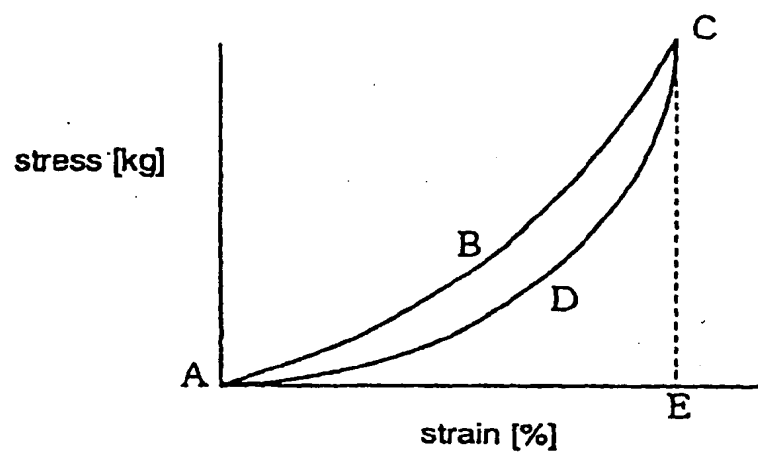


Fig.2

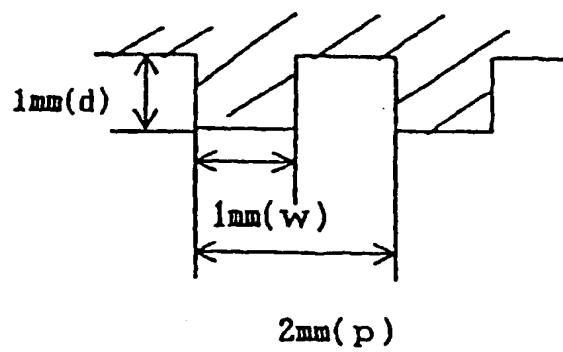
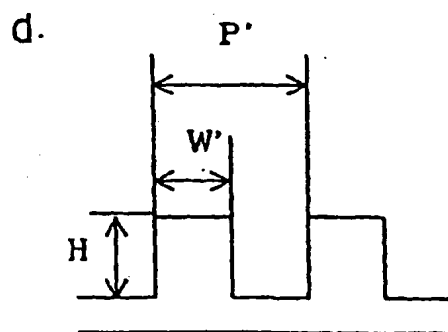
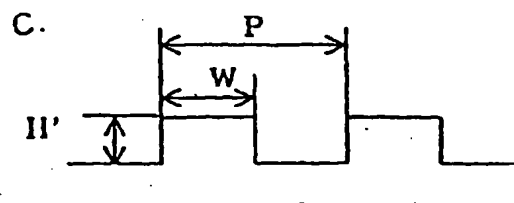
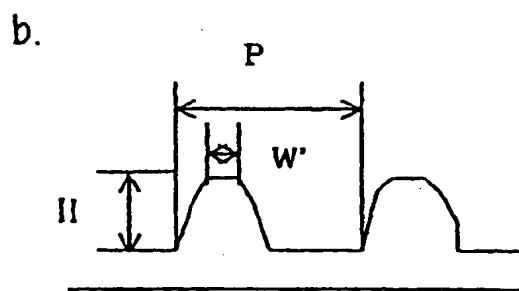
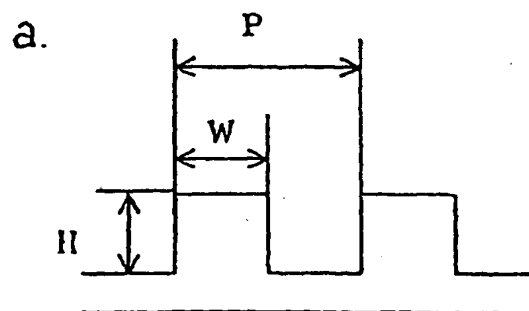


Fig.3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/03376

| A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ C08J9/36 | | |
|---|--|---|
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ C08J9/36 | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999 | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | JP, 57-20344, A (Mitsui Petrochemical Industries, Ltd.), 2 February, 1982 (02. 02. 82) & JP, 2-258247, A | 1-4 |
| A | JP, 7-137189, A (Sumitomo Chemical Co., Ltd.), 30 May, 1995 (30. 05. 95) (Family: none) | 1-4 |
| A | JP, 7-179624, A (Mitsui Petrochemical Industries, Ltd.), 18 July, 1995 (18. 07. 95) (Family: none) | 1-4 |
| A | JP, 52-3802, A (The Furukawa Electric Co., Ltd.), 12 January, 1977 (12. 01. 77) & JP, 57-10232, B2 | 1-4 |
| A | JP, 4-229258, A (Achilles Corp.), 18 August, 1992 (18. 08. 92) (Family: none) | 1-4 |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex. | | |
| * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family | | |
| Date of the actual completion of the international search 9 September, 1999 (09. 09. 99) | | Date of mailing of the international search report 21 September, 1999 (21. 09. 99) |
| Name and mailing address of the ISA/ Japanese Patent Office | | Authorized officer |
| Facsimile No. | | Telephone No. |

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/03376

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | JP, 55-98974, A (Kuraray Co., Ltd.), 28 July, 1980 (28. 07. 80) & JP, 59-43586, B2 | 1-4 |
| A | JP, 63-33430, A (Achilles Corp.), 13 February, 1988 (13. 02. 88) & JP, 4-5539, B2 | 1-4 |
| A | JP, 6-278220, A (Inoac Corp.), 4 October, 1994 (04. 10. 94) (Family: none) | 1-4 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)